PLA Improvement Using Nanocomposite and Plasma Modification

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Abstract

This work studied the effects of Oxygen (O_2), Nitrogen (N_2) and Air plasmas on the surface modification of Polylactic acid (PLA) films. PLA films with 0.01 mm thickness were prepared from pure PLA material, while the PLA nanocomposite was prepared by mixing pure PLA with 5.00 wt.% of Organoclay (Cloisit® 30B). The plasma discharge was operated by $-800\ V_{DC}$ of applied voltage at 0.1 mbar. The samples were placed on the substrate inside the plasma reactor and exposed to the plasma gases for 10, 15 and 20 min. The results showed that the hydrophobic property of pure PLA film can be increased by O_2 exposure for 10 min and air plasma exposure for 20 min. Whilst the hydrophilic properties of PLA nanocomposite film were elevated when exposed for 20 min to the air and N_2 plasma. In addition, PLA nanocomposite film has slightly higher levels of hydrophilic properties when compared to pure PLA film as evidenced by contact angle measurement. This result implies that low-temperature plasma discharges can successfully improve the surface property of PLA film in a short operating time.

Keywords: Low-temperature plasmas, PLA modification, Nanocomposite, Plasma modifications, Surface modifications

Introduction

Cold plasma processes for surface modifications utilize low temperature and are commonly used in a variety of applications such as biomedical, packaging, commercial materials and other applications. These surface modification processes can improve the surface and mechanical properties of materials (Borcia, 2013; De Geyter et al., 2010; Da Ponte, Sardella, Fanelli, d'Agostino, Favia, 2011; Oehr, 2003). The cold plasma can be generated at low pressure by direct current (DC), radio frequency (RF, typically frequency in ordered 1-100 MHz) and microwave (common frequency was 2.45 GHz) power sources. In the case of cold plasma at atmospheric pressure, this process can be generated by dielectric barrier discharges (DBDs) and operated by high-frequency alternating current (high-frequency AC, typically frequency in the range of 1-100 kHz) and RF power sources (Bogaerts, Neyts, Gijbels, & van der Mullen, 2002; Conrads & Schmidt, 2000). Plasma is an ionized gas and consists of electrons, neutral particles, free radicals, negative ions, positive ions, atoms and molecules. Whilst the interaction of the plasma on the material surfaces includes etching, functionalization, interstitial modification, deposition, sputtering and implantation, these reactions are well known in plasma research (Conrads & Schmidt, 2000; Eliezer, 2001).

Polylactic acid (PLA) is a friendly biodegradable polymeric material which has been widely used in agro-industries and health sciences such as food packaging and biomedical materials (that need these hydrophobic properties) and biocompatible materials. PLA is an interesting polymer because its fumes are non-toxic during incineration which also creates relatively low greenhouse gas emissions. However, PLA has low moisture transfer, high shrinkage and relatively low strength which need to be modified at low temperatures using cold plasma. The processes of PLA modification have been focused on biomedical, engineering and packaging applications.

There are many methods to modify the PLA such as incorporating the additives into PLA to make nanocomposites, nanophotography and plasma polymerizations (Armentano et al., 2013; De Geyter et al., 2010). When applying these methods, using plasma, the process is energy and cost-effective. Oxygen (O_2) and nitrogen (N_2) gases are widely used as reactive gases in plasma generation for surface treatments and polymer surface modifications. Junkar, Cvelbar, and Lehocký (2011) used O_2 and N_2 plasmas for surface treatment of polyethylene terephthalate (PET) polymer to alter the chemical composition. The results illustrated that the plasma treatment increased the surface roughness and wettability of PET. Similarly, O_2 plasma was also used for the surface improvement of polylactic acid (PLA), polyglycolic acid (PGA) and polysulfone (PSF) membranes. The results showed that hydrophilic (O-H and C=O) functional groups were obtained. After the plasma modification, the surface roughness increased, while the weight and surface diameter both slightly decreased while their tensile properties slightly changed (Fu & Zhang, 2019; Kaew-On, Chittrakarn, Ruangdit, Yuenyao, & Tirawanichakul, 2018). Similarly, PSF/PEG membrane was improved by Ar plasma. Similarly, hydrophilicity was enhanced with the increase in PEG dosage. Also, the polar groups of O-H and C-H bonds (hydrophilic property) were further increased on the membrane surface, while the morphological structures were also improved (Yuenyao, Chittrakarn, Tirawanichakul, & Sirijarukul, 2016). Furthermore, N_2 plasma was shown to modify PLA and PSF films (Richter et al., 2010; Yuenyao, Chittrakarn, Tirawanichakul, & Nakajima, 2017), and the hydrophilic property of both PLA and PSF films was improved as indicated by the decrease in the water contact angle.

This current work studied the improvement of PLA films using nanocomposite and plasma modification. The plasma gas was generated from surrounding gases (Oxygen (O_2), Nitrogen (N_2) and Air) and the effects on the surface and mechanical properties of the nanocomposite, and the type of plasma gas generated, were investigated.

Methods and Materials

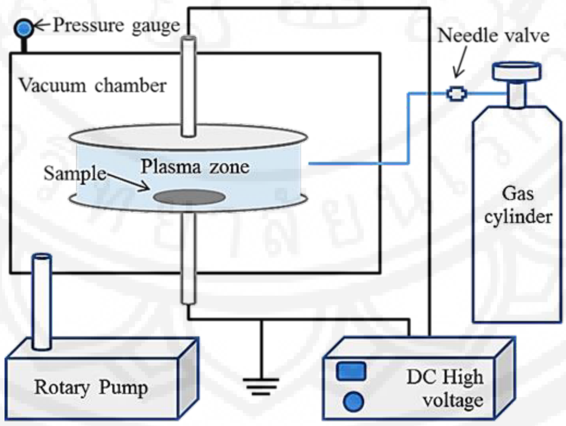

Figure 1 Schematic diagram of DC vacuum plasma for PLA surface modifications

The DC plasma system installed to study the surface modifications is shown in Figure1. This system was operated at low pressure by the negative DC high voltage to generate plasma through three types of gas (N_2, O_2, and air). The operating pressure was controlled by a needle valve and maintained by use of a rotary pump. Two stainless steel plates (inside the vacuum chamber) were used as an electrode to create the electric field and to generate a plasma gas in the plasma zone. The PLA sample was placed on the ground electrode.

To prepare pure PLA film, 5 g of PLA pellets were dissolved in 100 ml of chloroform and spread on a glass plate to a thickness of 0.01 mm. This sample was left to dry at room temperature for 24 hr. The film was then placed in an oven at 40°C for 24 hr, then left in the oven for a further 48 hr to eliminate the moisture at room temperature.

The same procedure was conducted to prepare the PLA nanocomposite film with 5.0 wt.% loading of Organoclay. Plastic pellets (4.75 g) and 0.25 g of Organoclays were dissolved in 100 ml of chloroform. Organoclay (Cloisit® 30B) is a nanoparticle with 13 µm particle size and 1.98 g/cm^3 density, with a specific gravity of 1.6. It has been used as an additive for rubber and plastic materials to improve physical properties such as strength, hardness, elasticity and water vapor permeation (WVP).

The operating conditions for this work were as follows. The vacuum chamber was cleaned at 2.50×10^{-2} mbar before gas feeding. Then the vacuum chamber was kept at 0.1 mbar with gas feeding of N_2, O_2 or air. The DC voltage was operated at -800 V while the power consumption was 20 W. Samples were exposed in the plasma zone for 10, 15 or 20 min.

Results and Discussion

After the samples were treated with any plasma gas, the surface and mechanical characterization for the samples were investigated, which included water vapor permeation (WVP) and water contact angle (WCA), tensile strength, elongation at break and Young's modulus. WCA was measured by the optical contact angle measuring instrument (Data Physics Instrument GmbH, model OCA15EC, Germany), while the measurement process for determining WVP was conducted following Rhim, Hong, and Ha (2009) Othman, Edwal, Risyon, Kadir, and Talib (2017) at 25°C and 50% relative humidity (RH), and the WVP was calculated using equation 1. Whilst the mechanical characterization was measured by the tensile and testing machine (Lloyd instrument, model: LRX). The measurement and determination processes are given according to the previous report by Dadbin, Naimian, and Akhavan (2011).

$$WVP = (\Delta m/\Delta t \cdot A)(L/\Delta p) \quad (1)$$

where $\Delta m/\Delta t$, A, L and Δp are the moisture weight gain (g/s), the surface area of the tested film (m^2), film thickness (m) and the difference of partial pressure (Pa), respectively. Fig. 2 shows the plasma generated by feeding different gases (Air, N_2 and O_2). Air and N_2 plasmas rather showed similar colors because the surrounding air consists of N_2 gas at about 70 vol.%. The intensity of the plasma colors implies the plasma properties of high density and temperature.

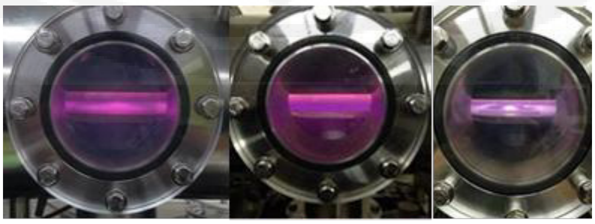

Figure 2 Plasma generated from the different gases

Surface Characterizations

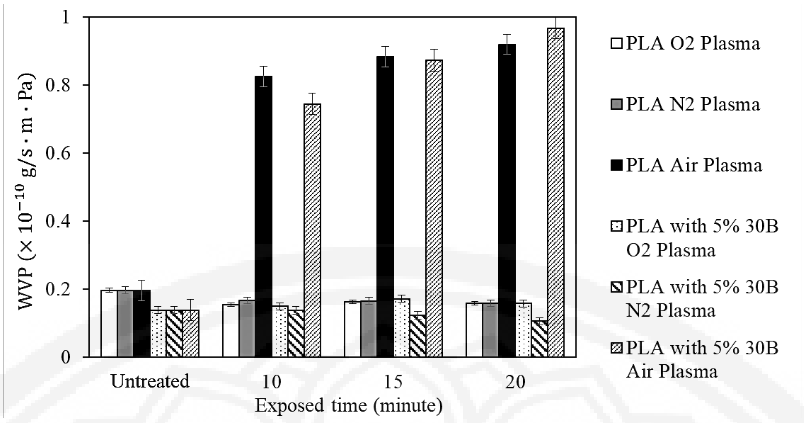

Figure 3 Effect of exposure time and plasma gases on WVP

In Figure 3, the untreated samples show that a PLA film with 5.0 wt.% of Organoclay (PLA with 5% 30B) sample has higher resistivity of WVP than a pure PLA (PLA) sample. This result indicates the main role of the added Organoclay in PLA film. Similarly, the effects of each plasma gas and exposure time on the WVP of PLA and PLA with 5% 30B samples are presented in Figure 3. The high value of WVP was found to result in a high hydrophilic property, whereas the low WVP values related to the good hydrophobic property. This shows that the air plasma enhanced the hydrophilic property of both sample surfaces, and the exposure time of 20 min resulted in higher property values than those of 10 and 15 min. These results support the application of PLA in biomedical fields.

In contrast, N_2 plasma enhanced the hydrophobic property of both samples, but especially for the PLA with 5% 30B treated by N_2 plasma at the exposure time of 20 min. This result illustrates that N_2 plasma enhances the surface roughness of the PLA film samples. This alteration was confirmed by measuring WCA in Figure 4. These results indicate that treatment in N_2 plasma is of interest for characterization by water contact angle measurement and mechanical analysis and can be applied to packaging materials.

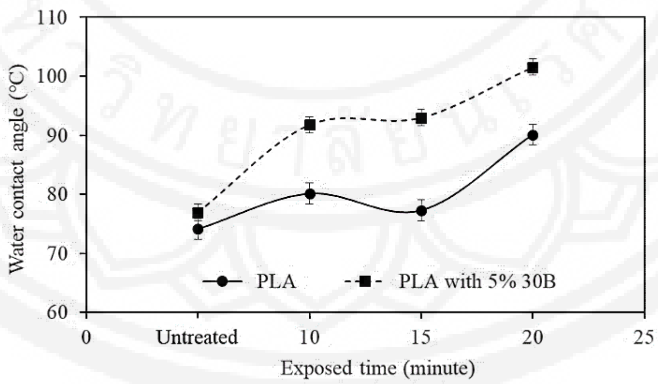

Figure 4 Effect of N_2 plasma treatment and exposure time on WCA measurement

In Figure4, the samples were investigated by measuring WCA after the samples were exposed to N_2 plasma for 10, 15 or 20 min. The results showed that the N_2 plasma and the exposure time have a great influence on increasing the value of WCA, especially in PLA with 5% 30B. At 20 min of exposure time, WCA of PLA with 5% 30B can reach up to 101.51°. As well, the relationship of the results illustrated in Figure 3 and Figure 4 represented the related WCA to WVP in which the high value of WCA indicated a good value for the hydrophobic property, whereas a low value of WCA shows a good value for the hydrophilic property. In addition, at 15 min of exposure time, the water contact angle of a pure PLA sample was decreased little, this event might be affected by a reverse of the roughness and polar functional groups on the surface. The relationship between WCA and roughness surface was discussed by Xu, Rajan, Chen, and Sarkar (2019).

Mechanical Characterizations

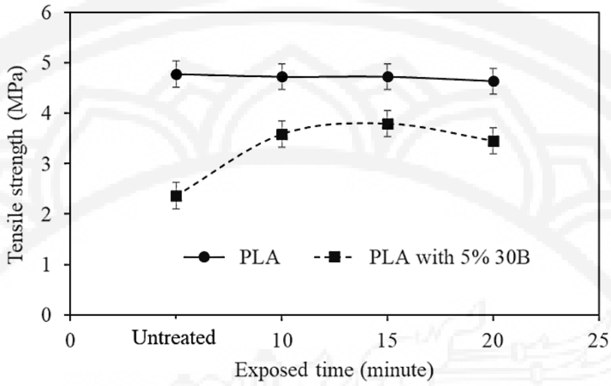

Figure 5 Effect of N_2 plasma treatment and exposure time on tensile strength

For mechanical property testing, the samples were tested for their tensile strength, elongation at break, and Young's modulus. The test results for tensile strength are shown in Figure 5 which illustrates that the untreated PLA has higher tensile strength than the untreated PLA with 5% 30B. However, after both PLA and PLA with 5% 30B were treated in N_2 plasma. N_2 plasma and exposure time did not influence the tensile strength in PLA but had the opposite effect of improving the tensile strength of PLA with 5% 30B, especially at 15 min. The testing of the elongation at break, illustrated in Figure 6, shows that PLA with 5% 30B resulted in the highest improvement of the elongation properties in N_2 plasma at 15 min whereas this treatment had a negative effect on PLA with a decrease in the elongation of PLA occurring at all exposure times. Young's modulus was applied in this testing to represent the elasticity of samples and, as shown in Figure 7, the results were that Young's modulus indicated that PLA can be improved by N_2 plasma at all exposure times, especially at 10 min of the exposure time. In the case of PLA with 5% 30B, this property cannot be improved by N_2 plasma at all exposure times.

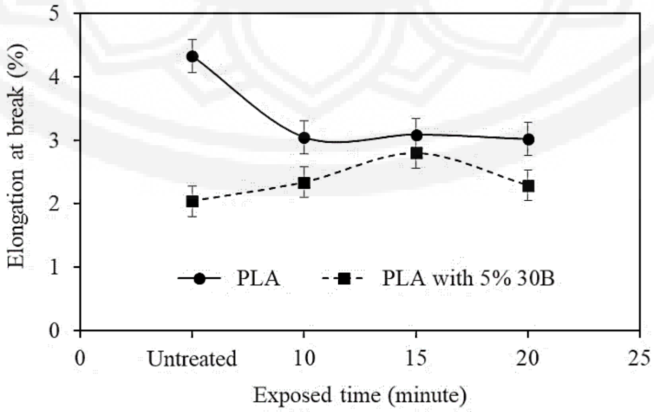

Figure 6 Effect of N_2 plasma treatment and exposure time on elongation at break

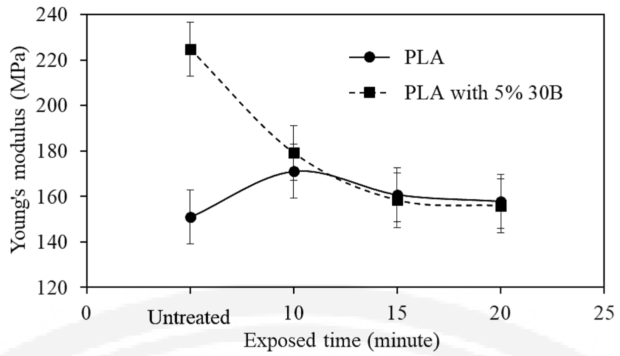

Figure 7 Effect of N_2 plasma treatment and exposure time on Young's modulus

Conclusion and Suggestions

This work has confirmed that the surface and mechanical properties of PLA and PLA with 5% 30B can be improved by exposure to several types of plasma gas and at different exposure times. Wettability (hydrophobic and hydrophilic) property was one of the surface properties that is improved by plasma treatment using the different plasma gases. Especially important is that most packaging materials need the hydrophobic property, so improving this property of PLA by adding 5 wt.% of Organoclay (Cloisit® 30B) and treating in N_2 Plasma is of considerable benefit in this application. In other applications, such as for biomedical materials which need the hydrophilic property, improvement of this property of both PLA and PLA with 5% 30B provides significant benefits also. Under the conditions tested, the WVP of both PLA and PLA with 5% 30B increased at all exposure times. In addition, Young's modulus of both PLA and PLA with 5% 30B can be improved by N_2 plasma at 10 min of exposure time.

Importantly, this research confirms that both PLA and PLA with 5% 30B, treated by N_2 plasma, are good materials for packaging applications.

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